<States and Structures> Polymer Condensed States

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Assoc Prof DI NOTO, Vito — University of Padova, Padova, Italy, 8 February 2002
Prof WHITE, James L — University of Akron, Akron, USA, 13 November 2002
Prof RISEN Jr, William M — Brown University, Providence, USA, 18 November 2002

Scope of Research

Attempts have been made to elucidate the molecular arrangement and the mechanism of structural formation/change in crystalline polymer solids, polymer gels and elastomers, polymer liquid crystals, and polymer composites, mainly by electron microscopy and/or X-ray diffraction/scattering. The major subjects are: synthesis and structural analysis of polymer composite materials, preparation and characterization of polymer gels and elastomeric materials, structural analysis of crystalline polymer solids by direct observation at molecular level resolution, and in situ studies on structural formation/change in crystalline polymer solids.

Research Activities (Year 2002)

Presentations

Structural analysis of the high-speed spun polyester fibers using the permanganic etching method, Yoshioka T, Tsuji M, Kawahara Y, et al., The 6th International Symposium organized by Inst. Chem. Res., Kyoto Univ. (ICRIS '02), January 31 - February 1 and other 4 presentations.

New insights into structural developments in natural rubber during uniaxial deformation by in-situ synchrotron X-Ray diffraction, Toki S, Murakami S, Kohjiya S, et al., Meeting of the Rubber Division, American Chemical Society, Savannah, Georgia, 29 April - 1 May.

Lamellar and crystalline-core thicknesses of the poly(3-oxotrimethylene) edge-on lamellae crystallized epitaxially from solution onto alkali halides, Tsuji M, Fujita M, Kohjiya S, Kawaguchi A, International Symposium on Polymer Crystallization, 9 - 12 June and other 2 presentation.

Biaxial tensile behaviors of elastomeric polymer networks, Kohjiya S, International Rubber Conference 2002, Prague, 3 July.

Volume phase transition of liquid crystalline gels, Urayama K, Okuno Y, Nakao T, et al., Polymer Networks 2002, France, 2 - 6 Sep, and related 6 presentations.

Conformational studies of an optically active 1,4-polyketone in solution and crystals, Kosaka N, Nozaki K, Tsuji M, et al., JSPS 51th Symposium on Macromolecules, 2 - 4 October, and other 3 presentations.

Devulcanization of unfilled natural rubber in supercriticl carbon dioxide, Kojima M, Tosaka M, Kohjiya S, Ikeda Y, 162nd ACS Rubber Division Meeting, Pittsburgh, 8 - 11 October.

Structure of band-like cellulose assemblies produced by acetobacter xylinum, Hirai A, Tsuji M, Horii F, 1st International Cellulose Conference, 6 - 8 November.

Structural Development of Natural Rubber during Uniaxial Stretching

Structural development of natural rubber during uniaxial stretching was examined by an in situ wide angle X-ray diffraction (WAXD) measurement using a synchrotron and simultaneous stress-strain measurement. During stretching, the amorphous halo remained clearly even at 500% strain (Figure 1). That is, some polymer chains were oriented and crystallized, but considerable fraction of the chains were not oriented at all in spite of large deformations of the specimen. This result indicates that only minor fraction of polymer chains contribute to the stress and hysteresis loss during elongation.

1. Murakami S et al., *Polymer*, **43**, 2117 (2002).
2. Toki S et al., *Macromolecules*, **35**, 6578 (2002).

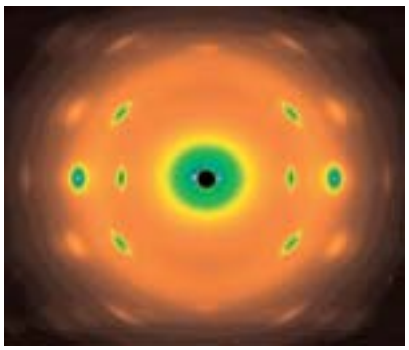

Figure 1. WAXD pattern of a natural rubber sample stretched up to 500% of the original length.

Volume Phase Transition of Liquid Crystalline Gels

We have firstly observed the volume phase transition of liquid crystalline (LC) gels accompanying the nematic-isotropic transition of LC molecules inside the gels[1]. The swelling of LC gels is mainly governed by nematic interaction, which is substantially different from the familiar swelling of isotropic gels mainly controlled by isotropic mixing interaction. Figure 2 displays the degree of equilibrium swelling as a function of temperature (T) for a LC gel in a low molar mass LC. Upon cooling, the isotropic swollen gel (a) is discontinuously transformed into the nematic shrunken gel (b) at T_{NI}^{G}. The nematic shrunken gel, surrounded by isotropic LC solvent, swells again in the region $T_{NI}^{S} < T < T_{NI}^{G}$. The nematic ordering of the surronding solvent at T_{NI}^{S} yields an inflection in the swelling curve without discontinuity. A mean field theoy successfully describes the complicated swelling and phase characteristics observed[2].

1. K. Urayama, Y. Okuno, T. Kawamura, S. Kohjiya, *Macromolecules*, **34**, 8252 (2001).
2. K. Urayama, Y. Okuno, T. Nakao, S. Kohjiya, *J. Chem. Phys.*, in press.

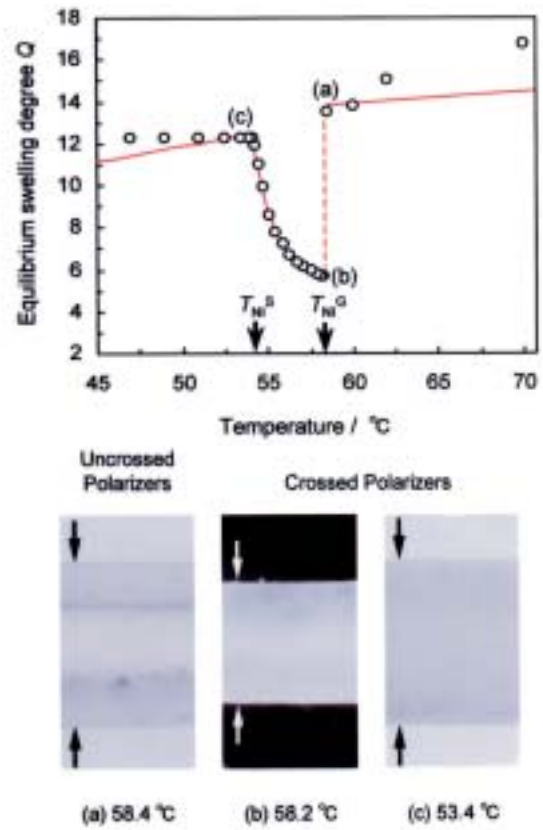

Figure 2. Equilibrium swelling - temperature curve of a nematic gel in a nematic solvent. The solid line represents the prediction of a mean field theory. The optical micrographs show the cylindrical gel in (a) totally isotropic phase; (b) nematic and isotropic phases inside and outside the gel, respectively; (c) totally nematic phase. The arrows indicate the boundary of the gel surface.

Grants

Kohjiya S, Role of polymers in all solid-state ionic devices, Grant-in-Aid for Scientific Research, Priority Area (B), 1 April 1999 - 31 March 2004.

Kohjiya S, Direct observation of amorphous polymer network structures by TEM, Grant-in-Aid for Scientific Research, (B)(2), 1 April 2001 - 31 March 2003.

Urayama K, Dynamics of guest polymers in host polymer networks, Grant-in-Aid for Scientific Research, Encouragement of Young Scientists, 1 April 2001 - 31 March 2003.

Tsuji M, Analysis of internal fine structure of the high-speed spun fibers for PET/PEN blends. Grant-in - Aid fir Scientific Research (C) (2), 1 April 2002 - 31 March 2004.